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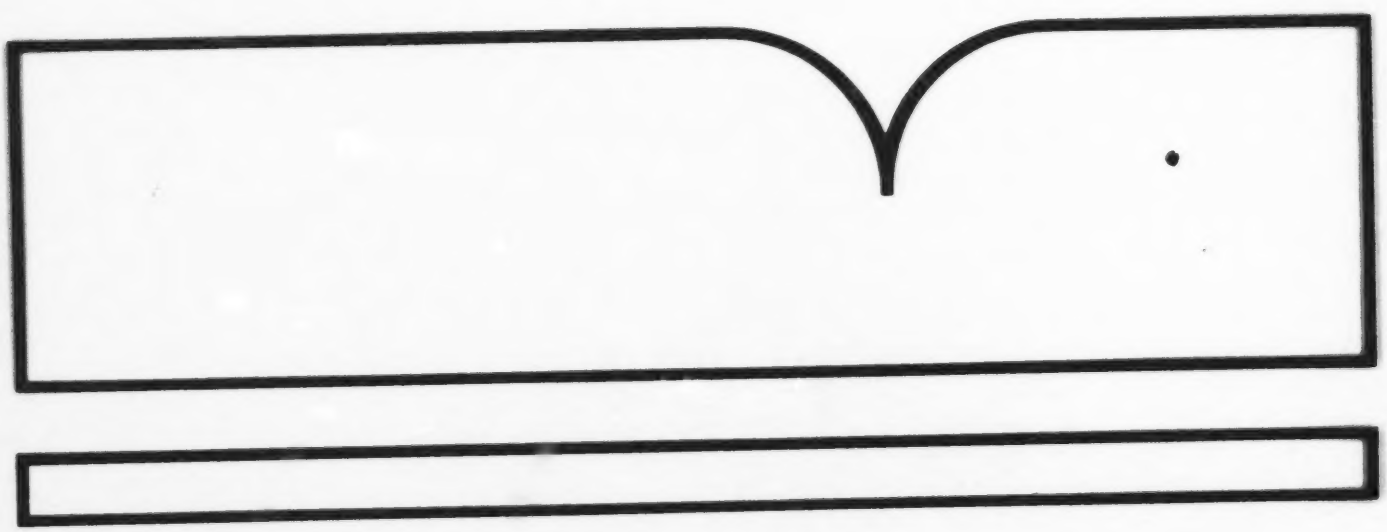

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HAZARDOUS WASTE DETOXIFICATION - SCIENCE AND TECHNOLOGY

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16. ABSTRACT

Current hazardous waste management practices in the United States are discussed. Changes in the management practices required by recent legislative amendments to both the Resource Conservation and Recovery Act and the Comprehensive Environmental Response, Compensation, and Liability Act are explained. Both established and emerging technologies are discussed. Limitations of these technologies and the opportunities for technology development are reviewed.

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HAZARDOUS WASTE DETOXIFICATION - SCIENCE AND TECHNOLOGY

SCOPE OF HAZARDOUS WASTE MANAGEMENT PRACTICES

Virtually every industrial activity generates waste. Today's laws require special handling and treatment of certain wastes. It is advantageous for industrial concerns to scrutinize their manufacturing processes that generate these materials with an eye toward waste reduction. Since many of these wastes place public health and/or the environment in jeopardy, they are classified under the federal Resource Conservation and Recovery Act (RCRA) as hazardous. Due to this designation, waste management practices in the United States are changing rapidly.

Significant efforts are now being made in the public and private sectors to either reduce the volumes of hazardous waste or to ensure that they are destroyed through adequate treatment processes. To tighten control of hazardous waste subject to regulation, RCRA's 1986 amendments lowered the exempted quantities of waste from 1000 kg/mo to 100 kg/mo for any manufacturing facility. While this did not drastically increase the quantity of wastes under regulation, it did expand by thousands the number of generators subject to this law.

A study done in 1981 shows that only 24% of the hazardous waste facilities in the United States were designed to actually treat these wastes. Of these installations, 69% simply stored the wastes, and 7% provided for disposal through land application (injection wells, surface impoundments and land fills). Figure 1 indicates the type of treatment facilities that existed in 1981. Not only was the quantity of wastes being treated relatively small, but many of these installations did not perform adequately to meet the standards being established for their waste streams.

The lack of treatment facilities, the large number of Superfund sites, and waste problems for which adequate treatment alternatives do not exist, provide a great incentive for EPA and the waste management industry to investigate and exploit emerging technologies that are more adaptable to these current problems. New technological approaches are necessary to avoid the reoccurring problems associated with past practices and have available a means to adequately treat the wastes we are generating today.

Forces Brought Forth by Recent Legislative Amendments to RCRA

The 1984 amendments to RCRA established a principle of restricting and minimizing the land disposal of hazardous wastes. These restrictions are significant and carry strict timetable "hammer dates." The so-called land ban restrictions set up a 5-year program to establish treatment standards that wastes must meet before being land disposed. A timetable for each group is given in Table 1.

The RCRA legislation requires mandatory notification of waste generation and the manifesting of waste shipments. These requirements and the permits required for storage, treatment, and disposal facilities have created cradle-to-grave control of these wastes. This situation has created a real opportunity for the development of adequate and cost effective treatment methods. For many of the wastes generated, a process to adequately treat them cost effectively or that has sufficient capacity to handle the waste volume is absent. This technology vacuum provides a true incentive and opportunity to develop and market new technologies.

Broader Basis of Action Due to Superfund Authority Reauthorization Act (SARA) of 1986

The SARA amendments of 1986 to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) legislation reauthorized the Superfund Program in the United States. The reauthorization established a new basis for conducting research and demonstration projects targeted to provide alternatives to clean up hazardous wastes sites. This research program includes laboratory investigations through scaled-up activities that provide actual demonstrations in the field. The Hazardous Waste Engineering Research Laboratory (HWERL) in Cincinnati, Ohio, has the role of developer and evaluator of suitable technology. The HWERL program is centered in a two-part Superfund Innovative Technology Evaluation (SITE) Program.

Major emphasis of the SITE Program is on technologies that are applicable and ready for full-scale demonstration at a Superfund site. Periodic solicitation of proposals and a competitive selection process form a basis to select technologies for field demonstration at full scale. Most often these demonstrations are done at a specific Superfund site. Through the SITE Program, the U.S. EPA arranges for the demonstration site, assists in permit requirements for the conduct of the demonstration, and underwrites the evaluation costs (analytical measurements). The technology developer is responsible for providing the equipment and the operational cost of that equipment during the demonstration. The intent of this program is to bridge the gap between undemonstrated methodology and its implementation and use. The SITE Program is currently evaluating 11 technologies; an additional 11 are being considered for demonstration in the near future. A list of these technologies is presented in Tables 2 and 3. The next solicitation of proposals for this program will be held in January 1988.

The SITE Program also provides assistance for the development of technologies. In this portion of the Program, technologies that are not yet ready for demonstration are selected. Although developmental projects requiring assistance have not yet been selected, plans have been made to do so in the next request for SITE proposals which will be conducted in December 1987. The next solicitation for demonstration projects will be in January 1988.

Early indications point to the SITE Program as an excellent means to promote and demonstrate emerging technologies. This aggressive program should add to the arsenal of technologies available for solving the hazardous waste problems in the United States.

SIGNIFICANT TRENDS IN THE MANAGEMENT OF HAZARDOUS WASTES [1]

Two major considerations are directing the way hazardous wastes are disposed of in the United States--legal liabilities and regulatory standards. Companies seeking to reduce or eliminate hazardous wastes that are generated by their manufacturing processes are doing so through process change, raw material substitution or reuse of waste materials. Industry is interested in treatment methods that will detoxify or destroy wastes thereby eliminating any potential future liability and not contribute problem residues. The public scrutiny of how wastes are to be handled or the permit requirements for the waste treatment facilities can result in lengthy delays. Public concern extends to the transportation or transfer point of wastes within a geographical area. As the populace becomes more informed and demands clean and credible waste management practices, significant economic reasons will be provided for the development of emerging detoxification technologies.

The 1986 RCRA amendments require the establishment of standards based upon the best demonstrated available technology (BDAT) for each waste stream. (The EPA, under CERCLA, is also establishing similar BDAT standards that will be

applicable to wastes at Superfund sites.) When one considers the various existing treatment technologies that can detoxify potentially hazardous wastes and the number of waste streams, one is confronted with a tremendous matrix of treatment technology vs. waste combinations. Good engineering judgment and common sense have led EPA to eliminate a number of these combinations for technologies not suited for a particular waste stream. Wastes have also been grouped into 22 categories having similar chemical and physical characteristics. By taking these two steps, the Agency has reduced the need to establish BDAT standards to a manageable number.

Best Demonstrated Available Technology Standards

To establish BDAT, EPA's preference is to go to an industrial establishment that has a treatment technology to be examined and produces the particular waste stream for which the standard is to be developed. Through a performance evaluation of that technology, the degree to which the waste can be treated will be determined. Evaluations of several potentially valid treatment processes will be made for a given waste stream. This quantitative information is then used by EPA's Office of Solid Waste to help establish a BDAT standard. It has been found that there are treatment plants presently treating waste streams producing a residue that will require further treatment to meet the new standard being established. The Agency is concerned not only with the residuals that will be going to the land but with air emissions and liquid effluents as well. New air emission standards are being developed. The effluent standards will depend on whether the discharge is direct to a water course or to a publicly-owned treatment works. A similar series of evaluations is being conducted on technologies for a variety of Superfund waste streams.

Once the Agency's BDAT levels have been established, it is likely that the waste treatment residuals will be required to pass three tests before they may be land disposed. The first test is the "paint filter" test. This is to ensure that the waste does not contain free moisture. The Agency is considering two further tests.

One test relates to the land-disposal restriction or BDAT number. For each hazardous component that may be present in a particular listed waste, EPA will establish the maximum concentration permissible in order for that waste to be disposed of on the land in a secure hazardous waste disposal facility. This maximum concentration will be the lowest concentration that can be achieved through treatment with the BDAT.

The other test is a proposed toxicity characteristic leaching procedure (TCLP) which evaluates the toxicity of constituent organics and metals. This test is to determine if the waste exhibits sufficiently low toxicity to be disposed of to the land in a non-secure land disposal facility. This TCLP contains a health-based limit for a number of organic compounds and metals. If the leachate from the TCLP contains concentrations in excess of the limits established for the TCLP, the waste must be further treated until it passes the test.

ESTABLISHED TECHNOLOGIES--THEIR PROBLEMS [2,3,4]

The conventional treatment processes available for industrial waste will provide, in the short term, some technologies useful to the remediation of hazardous waste sites. Unfortunately, reliable data on the performance of these technologies, for many hazardous waste streams, does not exist. Due to the complexity of the wastes and the matrices in which they are found at the many hazardous waste sites, there will be definite limitations to many treatment strategies. While some technologies of physical/chemical

and/or biological treatment have had major success with waterborne pollution, they remain to be established as effective technologies for the treatment of hazardous wastes. In many cases, the residuals from these processes continue to present problems. Other problems frequently experienced with existing technologies include: [5]

- Being limited to aqueous streams containing nonhalogenated contaminants;
- Not appropriate for solids or very viscous liquids;
- Relatively low temperatures may not be sufficient for halogenated wastes;
- Corrosion and fouling of equipment may reduce capacities;
- High pressures necessitate sophisticated equipment and operational techniques; and
- The products of reaction could be more hazardous than the original waste stream.

Physical/Chemical Processes

The use of incineration and related thermal technology offers treatment for many liquids and some contaminated solids substrates. It is the technology of choice for many solvents and other wastes with high BTU content. Thermal destruction is currently the required technology for dioxin wastes. When contaminants are in the soil, incineration can be accomplished but at a great cost.

The examples of ozonolysis and hypohalite oxidation give some insight into the available conventional chemical technology. Chemical oxidation by ozonolysis has been widely utilized in the water treatment of phenols, detergents, pesticides, and some inorganic species, i.e., cyanide, sulfide, and iron. Ozone has a major drawback in its short half-life and unfavorable mass transfer limitations between gas and aqueous phases. These restrictions

point to its general utility for oxygenating water in biodegradation systems but emphasize its limitations as a direct oxidant.

Advances have been made using ozonolysis as demonstrated by the paper included in this symposium from USDA Beltsville. Kearney and co-workers show the use of the combined technology of ozonolysis followed by microbial decomposition offer promise for the treatment of pesticide wastewaters containing herbicides such as atrazine and alachlor.

Disinfection by hypohalite oxidation is limited by the chemistry of the oxidant toward many organic compounds. Only easily oxidized compounds are susceptible to oxidation under these conditions. One major problem with hypohalites is that they can act as both oxidizing and halogenating agents thus frequently forming halogenated by-products which can possibly be more toxic than the parent compound.

Biological Processes

Few generalizations can be made concerning the biodegradation of toxic and hazardous wastes by conventional biological treatment [6]. The treatability of a particular waste stream is dependent on the unit processes of the treatment system. Treatability studies have attempted to assess the potential of a treatment system before the biodegradability of target compounds was established. Thus, apparent failure of a treatment system, under these circumstances, could not be attributed to inadequacies of the treatment system nor to the inability of the microflora to conduct the desired degradation of the target compounds. However, many biological systems are remarkably robust, having potential to degrade some of the more recalcitrant toxic and hazardous wastes. Success in these endeavors is based on the ability to discover ways to induce growth and utilization of the waste components by the treatment microorganisms. Survival of microorganisms is integral to the

treatment process despite the possible upset conditions encountered in normal operation where the influent is highly variable.

EMERGING TECHNOLOGIES--PROMISES AND LIMITATIONS [7]

These technologies are generally at a more basic stage of development as compared to those discussed in the previous section and have not been used commercially.

Chemical Processes

A substitution process involving the nucleophilic replacement of halides attached to aromatic ring structures appears very promising for treatment of haolgenated aromatics in the absence of water. The APEG process uses a reagent which is a mixture of sodium or potassium hydroxide solvated in a suitable polyethylene glycol. The process, to be described later in this symposium, has been successful in the detoxification of chlorinated aromatic compounds. Oils and sludges contaminated with dioxin have been successfully treated with this treatment system at Butte, MT, and Kent, WA. Soil detoxification by this technology is currently under investigation.

Photochemistry offers significant opportunities for the treatment of hazardous waste constituents. The nature of hazardous waste tends to narrow the range of photochemical technologies to rather clean waste streams. Colored bodies and other absorbing species with the waste tend to severely diminish the overall efficiency of the process. Promising work with semi-conductor mediated photolysis will be detailed later in this symposium. Solid phase photolysis is a treatment option in its very early stages of investigation. The use of photolytic treatment of soils and other solid matrices will require mechanical manipulation of the soil to expose new surfaces.

Alternative means to oxidize both organic and inorganic substrates, under non-thermal conditions, has not been systematically studied. Oxidation of organics with ruthenium tetroxide has been proposed as a means to destroy soil-bound organics. This detoxification technology will lead to additional contamination problems when applied to soil contamination. The use of more innocuous oxidants will probably be exploited in the near future. Treatment of ground water contamination using hydrogen peroxide has had a reasonable degree of success.

Biological Processes

For Superfund cleanups, biological detoxification is considered an emerging technology. The chemicals found contaminating Superfund sites persist for very good reasons. Many of the contaminants are toxic toward microorganisms and there are no significant environmental processes removing contaminants from the sites at an appreciable rate. These toxic chemicals are referred to as being recalcitrant since they are not utilized by the natural microflora as energy sources or merely transformed for detoxification purposes [8]. In many cases, microorganisms have not been able to develop the necessary cellular components to detoxify these man-made chemicals. While certain compounds continue to persist at waste sites, recent investigations have uncovered exceptional organisms having the ability to degrade these troublesome compounds. Recent successes include a series of organisms capable of degrading pentachlorophenol that is a major problem in the wood-treating industry. An organism isolated and studies by the General Electric Company and the University of Texas offers treatment for most of the PCB coengers. Continued development of this organism is proceeding to field scale soil testing. The ground water contaminant, trichloroethylene, has been the target of several groups for the discovery of degrading organisms. A number of

promising organisms have been isolated and shown to have remarkable competency toward trichloroethylene. These investigations are at the stage of bench-scale experimentation and will require scale-up. The exploitation of a wood-rotting fungus shows exceptional promise as both an in-situ soil detoxifier and a water treatment process. This technology will be discussed during this symposium. Techniques such as plasma-assisted molecular breeding continue to tantalize the biological detoxification effort with work leading to 2,3,5-T degraders. Most of the work in this area uses organisms selected from the environment for their specific abilities, without any genetic manipulations. The lack of public acceptance of recombinant organisms serves to delay the complete use of this technology for detoxification treatment.

Limitations

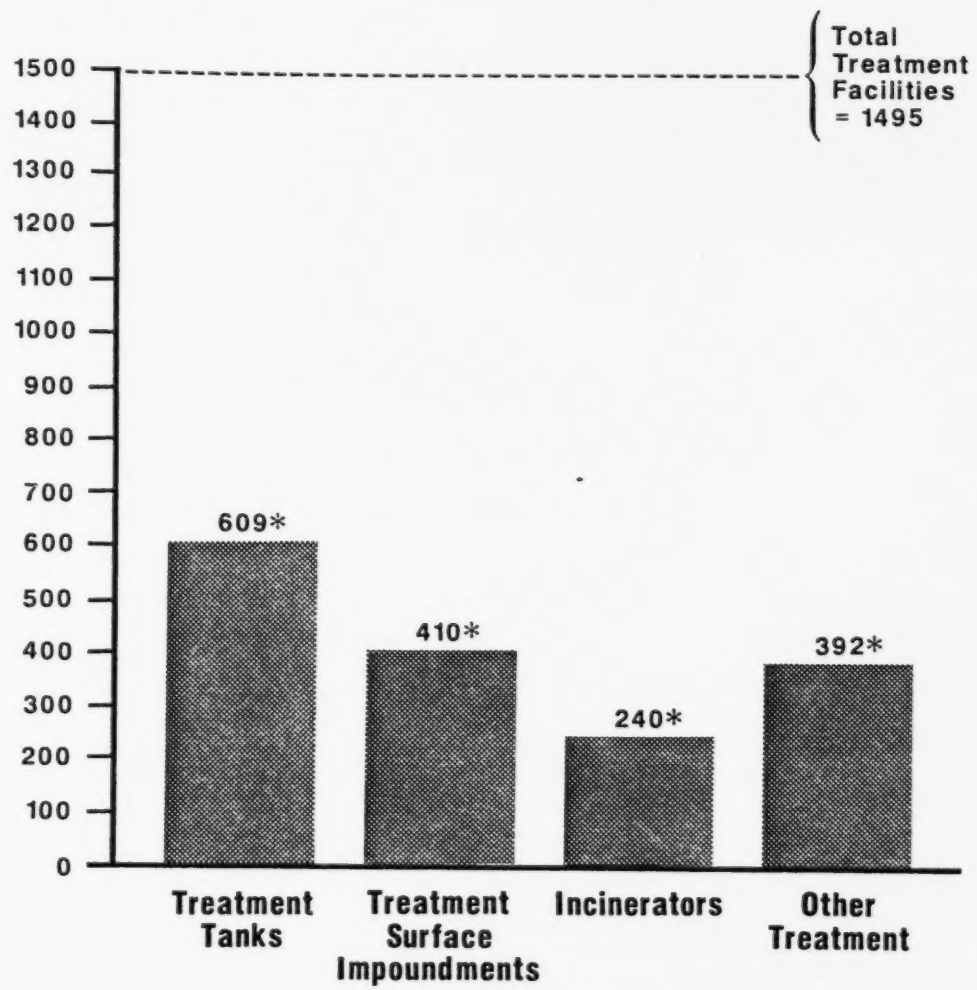
The ability of a treatment system to degrade or detoxify a waste stream is based inherently on favorable reaction kinetics and the corresponding mass transfer rates. Both conventional and emerging technologies are potentially limited by the formation of by-products. The significance of the by-products is seen in the context of toxicity. If a substrate molecule has been completely detoxified, the remaining steps between the by-product stage and final mineralization do not give rise to any new toxicity. Temperature can be an important ingredient in the overall success of a treatment technology. Rarely is there an opportunity to modify a treatment temperature given the variety of climate situations encountered across the United States. Technologies will be engineered to accommodate as many of the climate variations as possible.

SUMMARY

There are excellent opportunities for entry into the market of new technologies that can effectively treat the wide range of difficult hazardous waste cleanup problems. [9]

Anyone who has an interest in hazardous waste treatment research is encouraged to contact the Hazardous Waste Engineering Research Laboratory with their ideas or to volunteer to become associated with our programs. Individuals working in this field outside the Agency are welcome to participate in this research that eventually will provide viable alternatives for the destruction of hazardous materials in the United States.

Figure 1. Number of Facilities Treating Hazardous Waste In 1981, By Treatment Process Type



* Tanks + Impoundments + Incinerators + Other exceeds 1,495 because some facilities had more than one treatment type.

Table 1. Land Ban Restrictions Timetable.

Dioxins and Solvents	November 8, 1986
California List (Metals and Cyanides, Corrosives, Halogenated Orgaincs	July 8, 1987
First-Third of Remaining Hazardous Wastes	August 8, 1988
Second-Third of Remaining Hazardous Wastes	June 8, 1989
All Hazardous Wastes	May 8, 1990

Table 2. Current SITE Demonstration Technologies

Developer	Technology
American Combustion Technologies, Inc.	Pyreton Burner
Haztech/Shirco	Infrared Incinerator
Hazcon, Inc.	Solidification/Stabilization
Westinghouse	Pyroplasma
Westinghouse	Electric Pyrolyzer
Terra Vac, Inc.	In-situ Vitrification
New York State DEC	Plasma Arc
Ogden Environmental Services	Circulating Bed Combustor
Resources Conservation Company	Solvent Extraction Technology
GE and International Waste Technologies	In-situ Solidification
DETOX	Biological Process for Organics

Table 3. SITE Demonstrations Being Negotiated

Developer	Technology
IT International Technology Corp.	Aquifer Restoration System/In-situ Bioreclamation
Zimpro Environ. Control Systems	Pact TM Wastewater Treatment System
Retech, Inc.	Centrifugal Reactor with Plasma Heat
Soliditech, Inc.	Solidification Technology
DF Systems Corp.	Solvent Extraction Technology
Ecotech, Inc.	Liquid Solid Contact Digestion
Dorr-Oliver, Inc.	Oxitron Activated Carbon Fluid Bed Biological Systems
Waste Chem Corp.	Mobile Volume Reduction and Solidification System (VRS)
Chemfix Technologies, Inc.	Chemical Fixation/Stabilization (Metals)
Sanitech, Inc.	Removal of Toxic Metals from Contaminated Waters
Battelle Pacific Northwest Lab.	In-Situ Vitrification Technology

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